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(54) Process for firing ceramic honeycomb structural bodies.

(57) A ceramic honeycomb structural body-firing process includes the steps of: formulating a raw material from talc, kaolin and other cordierite-forming material to give cordierite having a chemical composition of SiO_2: 42-56% by weight, Al_2O_3: 30-45% by weight and MgO: 12-16% by weight as a main component and containing a crystalline phase mainly composed of cordierite, shaping a honeycomb structural body from the resulting mixture by extrusion, and firing the honeycomb structural body at a given temperature in a given atmosphere. In the firing step, a heating rate in a temperature range in which the honeycomb structural body is thermally shrunk is set at not less than 20°C/hr but not more than 60°C/hr, the heating rate in a temperature range in which the solid phase reaction of the honeycomb structure body proceeds is set at not less than 80°C/hr but not more than 130°C/hr, and the heating rate in a temperature range in which the liquid phase reaction of the honeycomb structural body proceeds is set at not less than 20°C/hr but not more than 60°C/hr.

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The present invention relates to a process for firing cordierite-based ceramic honeycomb structural bodies. In particular, the invention relates to the firing process suitabl for firing hon ycomb structural catalyst carriers having high strength and low thermal xpansibility and being adapted to be us d for the purification of exhaust gases from automobiles.

Heretofore, it is a conventional practice to produce cordierite-based ceramic honeycomb structural bodies by the steps of obtaining a ceramic body through formulating and mixing a cordierite-forming raw ceramic material with a shaping aid or a pore-forming agent, producing a ceramic honeycomb-shaped body by extruding the resulting ceramic body, and firing the ceramic honeycomb-shaped body at a given temperature in a continuous kiln or a periodic kiln.

Among others, the ceramic honeycomb structural bodies to be used as catalyst carriers for the purification of exhaust gases from automobiles must have a high water-absorbing rate to improve catalyst-carrying ability and a low coefficient of thermal expansion to improve thermal shock resistance. In order to attain appropriate values of the product characteristics, it is a conventional practice to control the maximum temperature and the holding time at the maximum temperature on firing.

Now, consider the case where the honeycomb structural body is produced by controlling the maximum temperature and the holding time as mentioned above. In order to increase the water-absorbing rate, since the porosity in honeycomb ribs needs to be increased, it is necessary to restrain the sintering through lowering the maximum temperature or shortening the holding time on firing. On the other hand, in order to lower the coefficient of thermal expansion, since the body needs to be densified, it is necessary to promote the sintering through raising the maximum temperature or prolonging the holding time on firing.

Therefore, both the high water-absorbing rate and the low coefficient of thermal expansion cannot be optimized only by controlling the maximum temperature and the holding time on firing. Further, since the characteristics of the product may largely change due to variation in properties of the raw materials, such as grain size or the average particle diameter, it is difficult to stably obtain various characteristics only by controlling the maximum temperature and the holding time.

On the other hand, Japanese patent application Laid-open No. 53-82,822 discloses a technique to attain a low coefficient of thermal expansion through the adjustment of the raw materials, in which the coefficient of thermal expansion can be lowered by increasing the heating rate in a temperature range of not less than 1,100 °C. However, this technique is insufficient from the standpoint of simultaneously attaining low thermal expansibility and high porosity.

It is an object of the present invention to solve the above-mentioned problems, and provide a process for firing ceramic honeycomb structural bodies of which product characteristics such as waterabsorbing rate and a coefficient of thermal expansion can be simultaneously optimized.

The present invention is directed to the ceramic honeycomb structural body-firing process including the steps of formulating a raw material from talc, kaolin and other cordierite-forming material to give cordierite having the chemical composition of SiO_2: 42-56% by weight, Al_2O_3: 30-45% by weight and MgO: 12-16% by weight as main components and containing a crystalline phase mainly composed of cordierite, shaping a green honeycomb structural body from the mixture by extrusion, and firing the green honeycomb structural body at a given temperature in a given atmosphere, wherein a heating rate in a temperature range in which the honeycomb structural body is thermally shrunk is set at not less than 20°C/hr but not more than 60°C/hr, the heating rate in a temperature range in which the solid phase reaction of the honeycomb structural body proceeds is set at not less than 80°C/hr but not more than 130°C/hr, and the heating rate in a temperature range in which the liquid phase reaction of the honeycomb structural body proceeds is set at not less than 20°C/hr but not more than 60°C/hr.

Heretofore, the heating schedule is that the temperature is raised to the holding temperature by a constant heating rate, for example, 60°C/hr. On the other hand, according to the heating schedule of the present invention, the heating rate is made not less than 20°C/hr but not more than 60°C/hr smaller than the conventional heating rate in the temperature range, e.g. about 1,100 to about 1,200°C, in which the honeycomb structural body is thermally shrunk, the heating rate is made not less than 80°C/hr but not more than 130°C/hr greater than the conventional heating rate in the temperature range,eg. about 1,200°C to about 1,300°C, in which the solid phase reaction of the honeycomb structural body proceeds; and the heating rate is made not less than 20°C/hr but not more than 60°C/hr smaller than the conventional heating rate in the temperature range, eg. about 1,300°C or more, in which the liquid phase reaction of the honeycomb structural body proceeds. The present inventors first discovered that the product characteristics, i.e. the high water-absorbing rate and the low coefficient of thermal expansion, which could not be simultaneously realized, can be satisfied by this heating sch dul .

That is, since the heating rate in the temperature range eg. about 1,100 to ab ut 1,200°C, causing the thermal shrinkage is set at n t less than 20°C/hr but not mor than 60°C/hr, th densification slowly proceeds

to attain the low coefficient of thermal xpansion. Further, since the heating rate is set at not less than 80°C/hr but n t more than 130°C/hr in the t mperatur range, g. about 1,200°C to ab ut 1,300°C, in which the solid phase reacti n proceeds, crystallization f undesirable cordierit , which will interrupt the crystallization f the cordierite in the succeeding liquid phase reaction as the main reaction, is suppressed in the solid phased-reacted state, and the low coefficient of thermal expansion and the high water-absorbing rate can be realized. In addition, since the heating rate is set at not less than 20°C/hr but not more than 60°C/hr in the temperature range, eg. not less than about 1,300°C to the holding temperature, in which the liquid phase reaction proceeds, the desirable cordierite is slowly crystallized in the liquid phasereacted state as the main reaction to attain the low coefficient of thermal expansion.

It is preferable that the heating rate is 30°C/hr - 50°C/hr in the thermal shrinkage temperature range, 90°C/hr - 110°C/hr in the solid phase reaction temperature range, and 30°C/hr - 50°C/hr in the liquid phase reaction temperature range.

The reason why the heating rate in the temperature range, eg. about 1,100 to about 1,200°C, in which the body shrinks is set at not less than 20°C/hr but not more than 60°C/h is that when the heating rate is slowed in this temperature range, the body is more slowly shrunk and densified to lower the coefficient of thermal expansion. Further, it is presumed that since the gaps between the particles of the raw material decrease with progress in the densification, the material is more easily converted to cordierite in the course of the liquid phase reaction to lower the coefficient of thermal expansion and increase the open porosity (waterabsorbing rate). If the heating rate in the thermal shrinkage temperature range is more than 60°C/hr, the coefficient of thermal expansion unfavorably becomes higher. Further, if the heating rate is set at not less than 80°C/h in this shrinkage temperature range, variation in dimension between upper and lower portions of the shaped body due to difference in temperature occurs in the shaped body. Thus, it is effective that the heating rate is slowed from this standpoint.

These and other optional features and advantages of the invention will be appreciated upon reading of the following description of the invention when taken in conjunction with the attached drawings, with the understanding that some modifications, changes and variations can be made by the skilled person in the art to which the invention pertains

For a better understanding of the invention, reference is made to the attached drawings, wherein:

Fig. 1 is a graph illustrating an ordinary heat curve and heat curves (1), (2) and (3) for examining the firing process of the present invention;

Fig. 2 is a graph illustrating an ordinary heat curve and heat curves (4), (5), (6) and (7) for examining the firing process of the present invention;

Fig. 3 is a graph illustrating an ordinary heat curve and heat curves (8), (9) and (10) for examining the firing process of the present invention; and

Fig. 4 is a graph illustrating an ordinary heat curve and heat curves (11), (12), (13), (14) and (21) for examining the firing process of the present invention.

The present invention will be explained more concretely with reference to the following examples.

Ceramic honeycomb-shaped bodies to which the firing process according to the present invention is applicable will be obtained typically as follows:

First, fine powders of talc, kaolin, alumina and other cordierite raw material are selectively formulated to give SiO_2: 42-56% by weight, preferably 47-53% by weight, Al_2O_3: 30-45% by weight, preferably 32-38% by weight, and MgO: 12-16% by weight, preferably 12.5-15% by weight around a theoretical cordierite composition point formerly known as the composition of a lower thermal expansion cordierite ceramics, and the formulated material is mixed and kneaded. Then, a shaping aid and/or a pore-forming agent is added into the resulting mixture to plasticize it to be extrudable, and the mixture is extruded into a honeycomb structural body. This shaped body is dried to obtain a green ceramic honeycomb structural body.

As the fine powdery talc, talc containing less alkaline component is particularly preferred. In making the powder of talc or kaolin finer, it is preferable to use calcined talc or calcined kaolin which is effective for the prevention of the cracking of the honeycomb structural body owing to the shrinkage on drying and firing. The calcined talc or calcined kaolin is adjusted to have the same average particle diameter as that of the raw material. As the shaping aid, an organic binder such as methyl cellulose, carboxymethyl cellulose, polyvinyl alcohol, starch paste, wheat powder, or glycerin, a surface active agent or wax may be selectively employed depending upon use. As the pore-forming agent, an appropriate one may be preferably selected among graphite, starch and wood chips.

Thereafter, the resulting green ceramic honeycomb-shaped structural body is fired under th ordinary conditions that the temperature is raised to the holding temperature, for example, 1,410°C at the ordinary heating rate of 60°C/hr except that the heating rate is n t l ss than 20°C/hr but not more than 60°C/hr in the temperature rang in which the honeycomb structural body is thermally shrunk; the heating rate is set at n t l ss

than 80°C/hr but not more than 130°C/hr in the temperature range of about 1,200°C to about 1,300°C in which th solid phas reaction proce ds; and the h ating rate is set at not less than 20°C/hr but not more than 60°C/hr in the temp rature rang of about 1,300 °C to about 1,400°C in which the liquid phase reaction proceeds.

In the following, examples of the present invention will be explained below.

Examples:

A ceramic raw material was obtained by formulating and mixing talc, kaolin and alumina raw materials to give a chemical composition of cordierite, and the mixture was plasticized by adding methyl cellulose thereto as a shaping aid. The plasticized mixture was shaped and dried to obtain a green honeycomb-shaped body having an elliptic cylindrical shape with 150 mm in major axis, 80 mm in minor axis and 150 mm in length. Such plural green honeycomb-shaped structural bodies having the same shape were produced.

First, in order to examine the influences of the heating rate upon the green honeycomb-shaped structural bodies, the honeycomb-shaped structural bodies were placed on a shelf in a muffle kiln, and fired while the heating rate was varied as shown in Table 1 with respect to the temperature range of about 1,100°C to about 1,200°C in which the honeycomb structural bodies thermally shrunk, the temperature range of about 1,200°C to about 1,300°C in which the solid phase reaction proceeded, and the temperature range of about 1,300°C to about 1,400°C in which the liquid phase reaction proceeded. Thereby, the honeycomb structural bodies were obtained. Various characteristics shown in Table 1 were measured with respect to the thus obtained honeycomb structural bodies, and influences on these characteristics were examined. After the temperature reached the holding temperature of 1,410°C by heating, the honeycomb structural bodies were held at this temperature for 4 hours, and cooled at a cooling rate of 150°C/hr.

The coefficient of thermal expansion was measured in a temperature range of 40-800°C in a honeycomb-extruded direction. The water-absorbing rate was measured in such a manner that the honeycomb structural body was dipped into an aqua at 30°C for 2 minutes for simulation of carrying a catalyst, excess water was removed with compressed air at a rate of 1.4 kgf/cm^2, and the coefficient of water absorbed was determined as a weight percentage relative to a weight of the dried honeycomb structural body, i.e., {(weight after water absorption - dried weight)/ dried weight} x 100. For the evaluation of the thermal shock resistance, the temperature which cracked the honeycomb structural body and thus caused sonant on hitting in the case where the honeycomb structural body was taken out from an electric furnace to room temperature after the honeycomb structural body was heated to this temperature step by step (25°C by 25°C from 700°C) in the electric furnace, while the honeycomb structural body was held at each 20 minutes. Results are shown in Table 1.

Table 1

Heating curve		Ordinary firing	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)
Heating rate (°C/Hr)	1100-1200°C	60	20	80	120	60	60	60	60	60	60	60
	1200-1300°C	60	60	60	60	20	80	110	130	60	60	60
	1300-1400°C	60	60	60	60	60	60	60	60	20	80	120
Water-absorbing rate(%)		18.3	19.0	17.7	17.5	17.0	18.7	19.5	18.7	18.0	18.5	19.0
porosity(%)		39.2	39.7	38.7	38.4	38.0	39.4	40.1	39.4	38.7	39.3	39.7
Coefficient of thermal expansion($\times 10^{-6}$/°C)		0.55	0.52	0.60	0.70	0.75	0.48	0.43	0.48	0.50	0.62	0.65
Thermal shock-resisting temperature(°C)		800	850	775	750	700	875	925	875	875	775	775

Table 1 shows the results of various characteristics of the honeycomb structural bodies fired according to the ordinary heat curve, and the heat curves (1), (2) and (3), and it is seen that when the heating rate in the temperature range of about 1,100°C to about 1,200°C is slowed, the coefficient of thermal expansion tends to decreas and the water-absorbing rat (porosity) tends to increas , and that xcell nt characteristics can be obtained when the heating rate in this temperature range is set at not less than 20°C/hr but not more than

60°C/hr.

Table 1 also shows the results of various characteristics of the honeycomb structural bodies fired according to the ordinary heat curve, and the heat curves (4), (5), (6) and (7), and it is seen that when the heating rate in the temperature range of about 1,200°C to about 1,300°C is raised, the coefficient of thermal expansion tends to decrease and the waterabsorbing rate (porosity) tends to increase, and that excellent characteristics can be obtained when the heating rate in this temperature range is set at not less than 80°C/hr but not more than 130°C/hr.

Table 1 further shows the results of various characteristics of the honeycomb structural bodies fired according to the ordinary heat curve, and the heat curves (8), (9) and (10), it is seen that when the heating rate in the temperature range of about 1,300°C to about 1,400°C is lowered, the coefficient of thermal expansion tended to decrease, and that excellent characteristics can be obtained when the heating rate in this temperature range is set at not less than 20°C/hr but not more than 60°C/hr.

In view of the results given in Table 1, it was presumed that the heat curve would be excellent in which the heating rate in the temperature range of about 1,100°C to about 1,200°C is not less than 20°C/hr but not more than 60°C/hr, the heating rate in the temperature range of about 1,200°C to about 1,300°C is not less than 80°C/hr but not more than 130°C/hr and the heating rate in the temperature range of about 1,300 °C to about 1,400°C is not less than 20°C/hr but not more than 60°C/hr. Based on this presumption, honeycomb-shaped structural bodies were actually fired according to heat curves specified in Table 2, and characteristics were examined with respect to the thus obtained honeycomb structural bodies in the same manner as in Table 1. Results are shown in Table 2.

Table 2

Heat curve		Ordinary firing	(11)	(12)	(13)	(14)	(15)	(16)	(17)	(18)	(19)	(20)	(21)
Heating rate (°C/Hr)	1100-1200°C	60	60	50	30	20	60	60	60	60	60	60	40
	1200-1300°C	60	80	80	80	80	90	110	130	80	80	80	100
	1300-1400°C	60	60	60	60	60	60	60	60	20	30	50	40
Water-absorbing rate(%)		18.3	18.7	19.0	19.1	18.7	19.4	19.5	18.7	18.7	19.2	19.3	19.8
Porosity(%)		39.2	39.4	39.7	39.9	39.4	40.5	40.1	39.4	39.4	40.1	39.9	40.6
Coefficient of thermal expansion($\times 10^{-6}$/°c)		0.55	0.48	0.45	0.46	0.49	0.43	0.43	0.48	0.48	0.44	0.44	0.40
Thermal shock-resisting temperature(°c)		800	875	900	985	870	930	925	875	875	910	915	950

It is seen from the results in Table 2 that the honeycomb structural bodies fired according to the heat curves (11)-(21) exhibit more excellent results with respect to all the examined characteristics as compared with those

fired according to the heat curves (1) through (10) in Table 1. In order to clarify the features of the heat curves, th h at curves in Tables 1 and 2 are illustrated in Figs. 1 through 4. Fig. 1 sh ws the ordinary heat curv , and the heat curv s 1, 2 and 3. Fig. 2 shows the ordinary heat curve, and the heat curves 4, 5, 6 and 7. Fig. 3 shows the ordinary heat curve, and the heat curves 8, 9 and 10. Fig. 4 shows the ordinary heat curve, and the heat curves 11, 12, 13, 14 and 21.

NGK discloses in Japanese patent application laid-open No. 2-255,576 that the honeycomb structural body having excellent dimension accuracy can be obtained by setting the heating rate at not more than 60°C/hr in the temperature range of about 1,100 to about 1,200°C in which the ceramic honeycomb structural body is thermally shrunk and in which rise in temperature of the honeycomb structural body is stopped for a given period. When this technique is combined with the present invention, the honeycomb structural body having excellent product characteristics and excellent dimension accuracy can be obtained. Thus, such a combination of the 20-60°C/hr heating and the stopping of the temeprature rise in the honeycomb structural body-shrinkage temperature range is included in the present invention.

As is clear from the above explanation, according to the ceramic honeycomb structural body-firing process of the present invention, the heating rate in the temperature range in which the cordierite-based honeycomb structural body is thermally shrunk is set at not more than 60°C/hr, the heating rate in the temperature range in which the solid phase reaction proceeds is set at not less than 80°C/hr, and the temperature range in which the liquid phase reaction proceeds is set at not more than 60°C/hr. Thereby, the ceramic honeycomb structural bodies having a low coefficient of thermal expansion and a height water-absorbing rate can be obtained, while undesirable crystallization of cordierite is being prevented. Further, various properties of the honeycomb structural bodies can be stably and excellently exhibited by varying the heating rates in the above three temperature ranges in appropriate combination, even when the composition of the raw materials varies.

Claims

1. A ceramic honeycomb structural body-firing process comprising the steps of: formulating a raw material from talc, kaolin and other cordierite-forming material to give cordierite having a chemical composition of SiO_2: 42-56% by weight, Al_2O_3: 30-45% by weight and MgO: 12-16% by weight as a main component and containing a crystalline phase mainly composed of cordierite, shaping a honeycomb structural body from the resulting mixture by extrusion, and firing the honeycomb structural body at a given temperature in a given atmosphere, wherein a heating rate in a temperature range in which the honeycomb structural body is thermally shrunk is set at not less than 20°C/hr but not more than 60°C/hr, the heating rate in a temperature range in which the solid phase reaction of the honeycomb structural body proceeds is set at not less than 80°C/hr but not more than 130°C/hr, and the heating rate in a temperature range in which the liquid phase reaction of the honeycomb structural body proceeds is set at not less than 20°C/hr but not more than 60°C/hr.

2. The firing process according to claim 1, wherein said heating rate in the temperature range in which the honeycomb structural body is thermally shrunk is set at not less than 30°C/hr but not more than 50°C/hr, the heating rate in the temperature range in which the solid phase reaction of the honeycomb structural body proceeds is set at not less than 90°C/hr but not more than 110°C/hr, and the heating rate in the temperature range in which the liquid phase reaction of the honeycomb structural body proceeds is set at not less than 30°C/hr but not more than 50°C/hr.

3. The firing process according to Claim 1, wherein the chemical composition is SiO_2: 47-53% by weight, Al_2O_3: 32-38% by weight and MgO: 12.5-15% by weight.

FIG_1

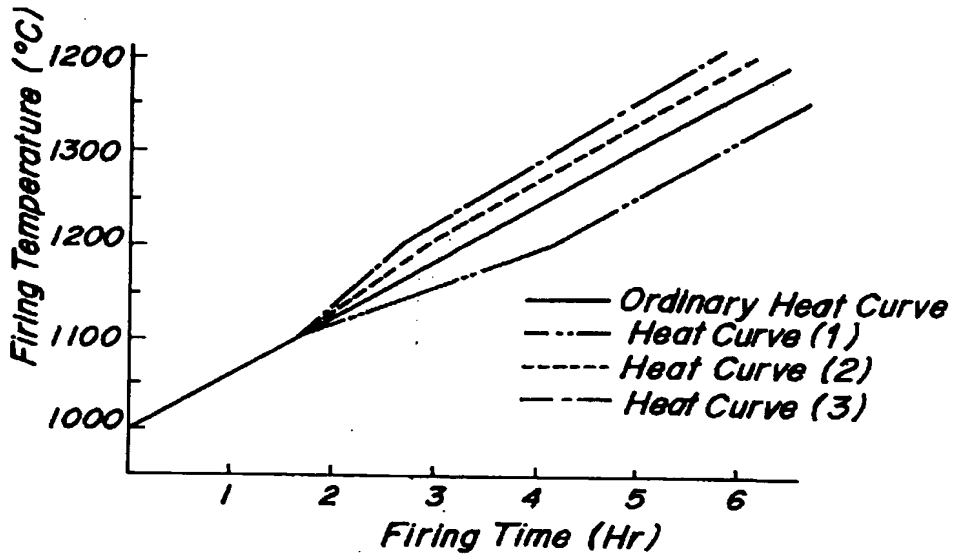

Firing Temperature (°C)
1200
1300
1200
1100
1000
1
2
3
4
5
6
Firing Time (Hr)
Ordinary Heat Curve
Heat Curve (1)
Heat Curve (2)
Heat Curve (3)

FIG_2

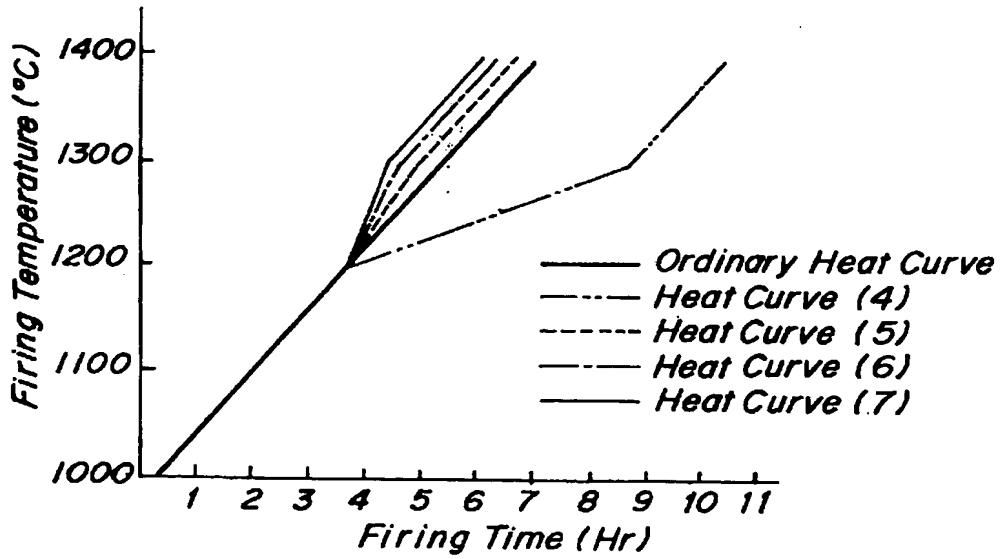

Firing Temperature (°C)
1400
1300
1200
1100
1000
1
2
3
4
5
6
7
8
9
10
11
Firing Time (Hr)
Ordinary Heat Curve
Heat Curve (4)
Heat Curve (5)
Heat Curve (6)
Heat Curve (7)

FIG_3

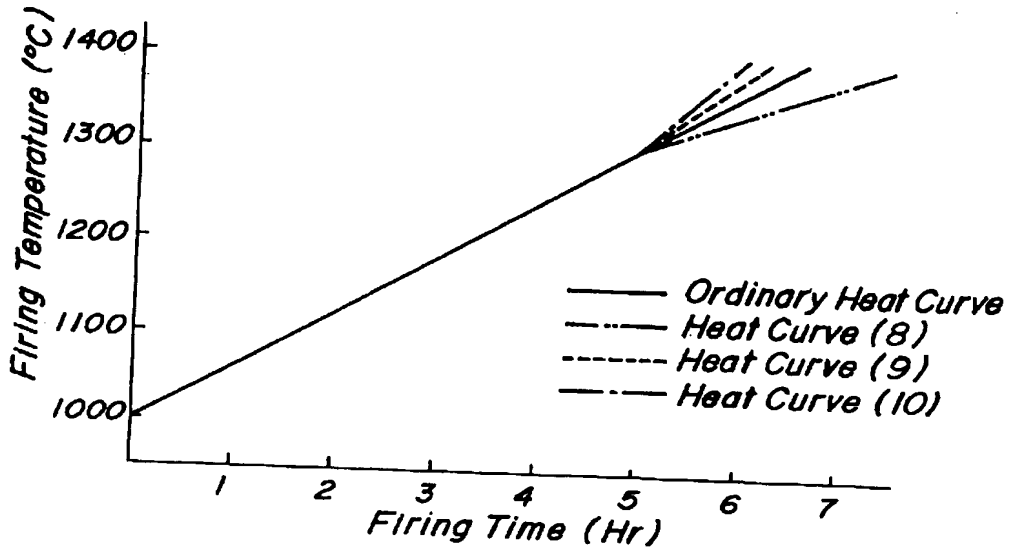

Firing Temperature (°C)
1400
1300
1200
1100
1000
1
2
3
4
5
6
7
Firing Time (Hr)
Ordinary Heat Curve
Heat Curve (8)
Heat Curve (9)
Heat Curve (10)

FIG_4

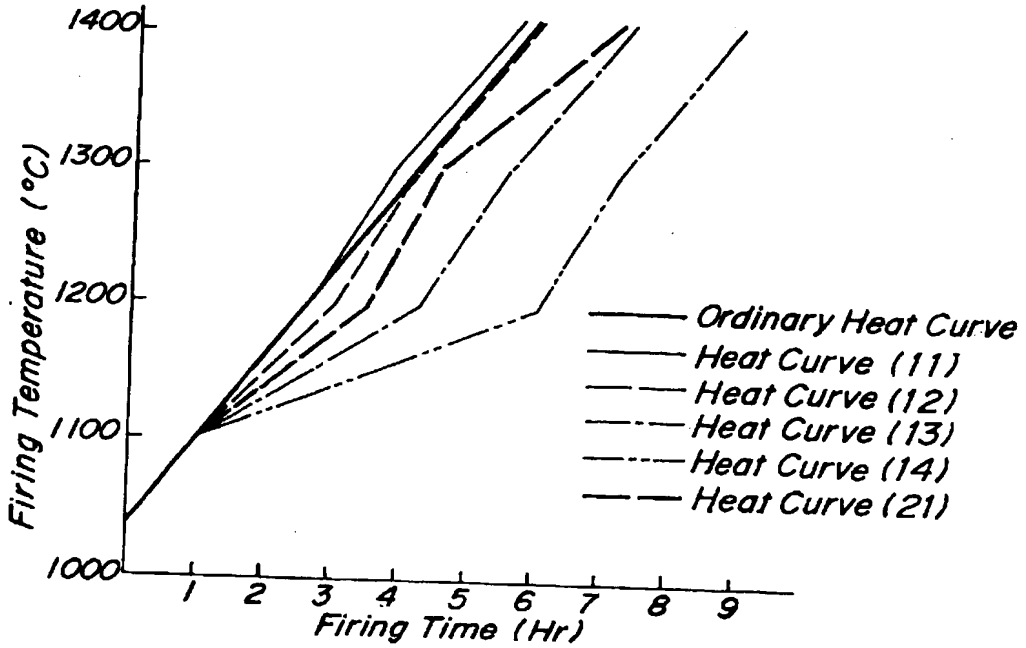
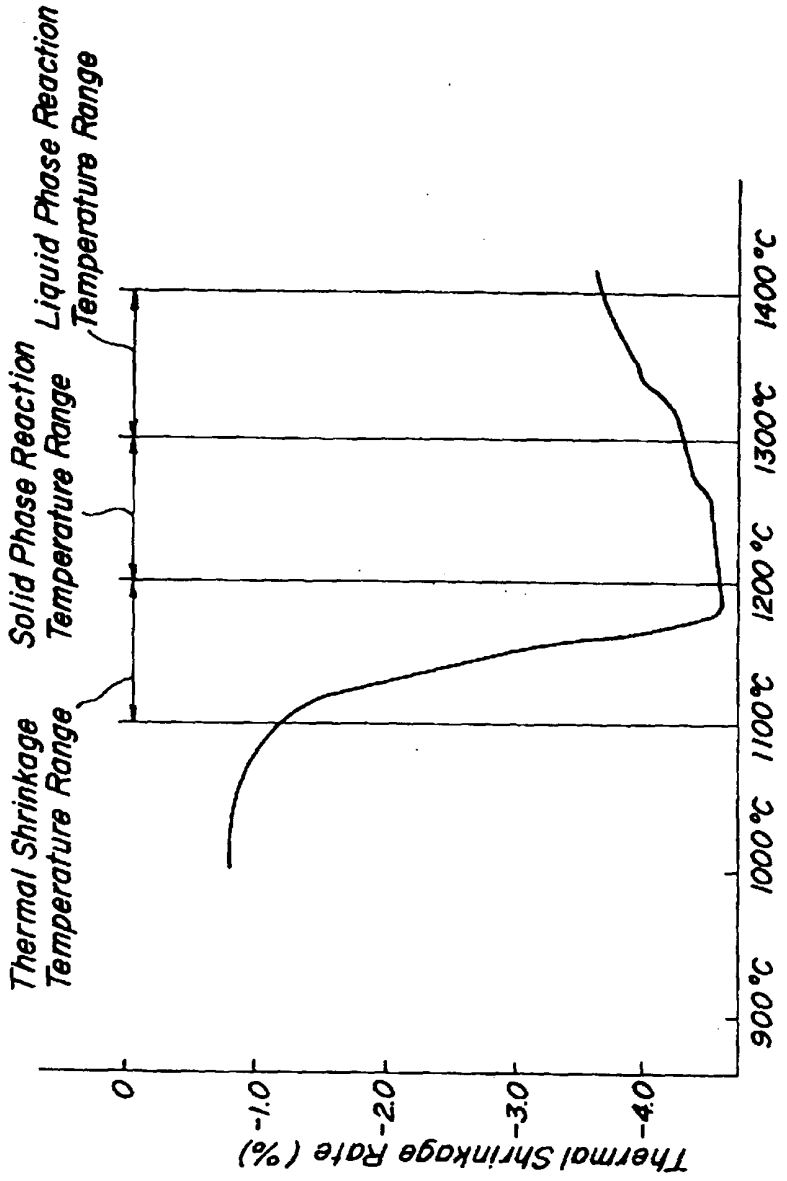

Firing Temperature (°C)
1400
1300
1200
1100
1000
1
2
3
4
5
6
7
8
9
Firing Time (Hr)
Ordinary Heat Curve
Heat Curve (11)
Heat Curve (12)
Heat Curve (13)
Heat Curve (14)
Heat Curve (21)

FIG_5


Thermal Shrinkage Temperature Range
Solid Phase Reaction Temperature Range
Liquid Phase Reaction Temperature Range
Thermal Shrinkage Rate (%)
0
-1.0
-2.0
-3.0
-4.0
900°C
1000°C
1100°C
1200°C
1300°C
1400°C

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 92 30 8749

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
A	US-A-5 046 946 (K. YASUDA ET AL.) * column 3, line 3 - line 18; claims 1-2; figure 1 *	1-3	C04B35/18 C04B35/64 B01J21/14
A	EP-A-0 227 482 (NGK INSULATORS, LTD.) * claims 5,6 *	1-3	
A	EP-A-0 232 621 (NGK INSULATORS, LTD.) * page 5, line 21 - line 27; example 1 *	1-3	

TECHNICAL FIELDS SEARCHED (Int. Cl.5)

C04B
B01J

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	07 DECEMBER 1992	LUETHE H.

CATEGORY OF CITED DOCUMENTS

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